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Preparation of Ti6Al4V/BG/HA graded coating by electrophoresis deposition in absolute alcohol medium①

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[Abstract] A codeposition of bioglass (BG) and hydroxyapatite (HA) on the substrate Ti6Al4V is realized in a non-aqueous solution system by inducing crystallization of HA on surface of the BG grain and electrophoresis deposition (EPD), and then a bioactive graded ceramic coating was obtained after sintering of the coating. This technique is a new method for making bioactive graded coating. The adhesive strength between the coating and the substrate reaches 18 MPa, and the better electrophoresis depositing parameters and optimal sintering procedure are obtained.

[Key words] hydroxyapatite; bioglass; electrophoresis deposition; graded coating; titanium alloy
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1 INTRODUCTION

Hydroxyapatite (HA), a major inorganic salt composition in human bone, has excellent biocompatibility, so it can combine with bone tissue well in chemical bond after it is implanted into human body[1,2]. It is a good bone filler and replacement material; but because of its brittleness it is not appropriate to be taken as replacement material of a load bearing bone[3]. One of the ways for resolving this problem is to coat it on some biomedical metal materials having good toughness, so that the synthesis advantages of the two kinds of materials can be utilized[4,5]. However, because of the difference of thermal expansion coefficient between HA and the substrate, HA coating often fails[6,7].

Titanium and its alloy (Ti6Al4V) implants are widely used in orthopaedic and dental surgery recently[8]. In this study, the bioglass (Na_2O-CaO-SiO_2-P_2O_5 system)[9] with a coefficient of thermal expansion similar to that of Ti6Al4V was chosen as raw materials, and the electrophoresis deposition was used to prepare a graded ceramic coating on the Ti6Al4V substrate.

2 EXPERIMENTAL

2.1 Design of graded coating

Na_2O-CaO-SiO_2-P_2O_5 system bioglass (BG), which has lower melting point, was taken as a binder at high temperature. A graded composition distribution of the BG and HA in the coating was helpful to reduce the innerstress and improve adhesive strength of the coating. The surface of the BG grain was modified by inducing crystallization of HA, which can change the charge characteristics of the BG powder and realize the codeposition of the BG and HA on the Ti6Al4V substrate. The schematic diagram of the designed graded coating is shown in Fig. 1.

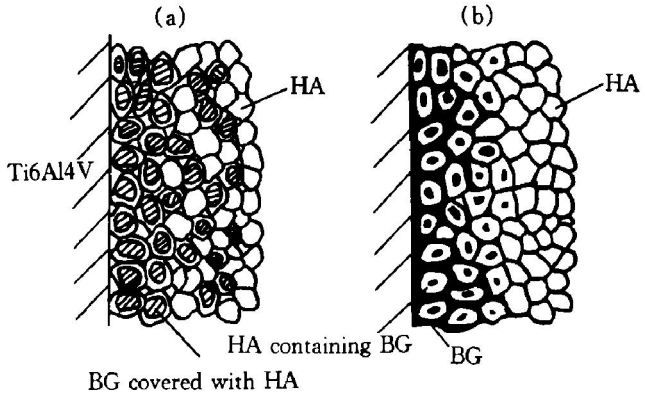

Fig. 1 Schematic diagram of designed graded coating (a) —Before sintering; (b) —After sintering

2.2 Preparation of raw materials

After being melt, quenched in water and milled by a jet mill, the bioglass was classed through gravity settling, and then the BG powder less than 2 μm was dispersed in 0.005 mol/L $Ca(NO_3)_2$ solution to get a $Ca(NO_3)_2$ suspension of the BG powder. Drop 0.003 mol/L $(NH_4)_2HPO_4$ and $NH_3 \cdot H_2O$ into the suspension, control temperature at 40~ 50 ℃ and pH value at 11~ 12 while stirring the suspension constantly. And the following reaction was taken place:

$$10Ca(NO_3)_2 + 6(NH_4)_2HPO_4 + 8NH_4OH \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + 20NH_4NO_3 + 6H_2O$$

The reaction lasted 6 h, then the reaction solution was aged for one week. After removing some

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floater on the surface of the solution, filtering and washing with distilled water, subsequently milling in a ball mill pot added with absolute alcohol medium, a colloid suspension was prepared.

2.3 Electrophoresis deposition

Titanium alloy (Ti6Al4V) flakes, serve as cathodes, were polished and washed with acid, cleaned by ultrasonic in acetone solution, and then washed with distilled water again and dried in air. Platinum flakes were taken as anodes. After the 6g/L suspension containing the BG powder was dispersed for 30min, the two electrodes were inserted into the suspension with distance of 1cm and voltage of 50V. After depositing for 30s the absolute alcohol suspension of HA was added into the BG suspension drop by drop. After codepositing for 1~ 7min, the coated cathode was taken out from the electrophoresis cell and dried in desiccator.

2.4 Sintering

The coated and dried samples were sintered in a pipe furnace under flowing high-purity argon gas. The sintering temperature was in the range of 850~ 1000 ℃, the soak time was 1h, the heating rate was less than 3 ℃/min and the cooling rate was less than 2 ℃/min.

2.5 Test and analysis

Particle sizes of the BG and HA powder were measured by the electrophoresis granulometer. The coefficient of thermal expansion of the sintered bodies of the BG powder and the titanium alloy were tested by quartz dilatometer. Chemical and mineral composition of the modified BG powder and the coating were analyzed by IR and XRD. Surface and cross section appearances of the coating were observed by SEM.

3 RESULTS AND DISCUSSION

3.1 Composition and properties of modified BG powder

The particle size of the modified BG powder is less than 3μm, coefficients of thermal expansion of the BG powder and Ti6Al4V are 9.9×10^{-6}/℃ and 10.3×10^{-6}/℃ in the temperature range of 30~ 1000 ℃, respectively.

From the XRD pattern (as shown in Fig. 2) of the modified BG powder, it is verified that the main crystal phase is HA. In the IR patterns (as shown in Fig. 3), the extra peak at 3570cm^{-1} corresponds to the stretch vibration of O—H in OH^-, the peaks at 1100cm^{-1}, 870cm^{-1}, 602cm^{-1} and 1035cm^{-1} are just the feature peaks of PO_4^{3-} [10], the peaks at 3439cm^{-1} (3437cm^{-1}) and 1631cm^{-1} (1632.56 cm^{-1}) belong to the shrink vibration and inflection

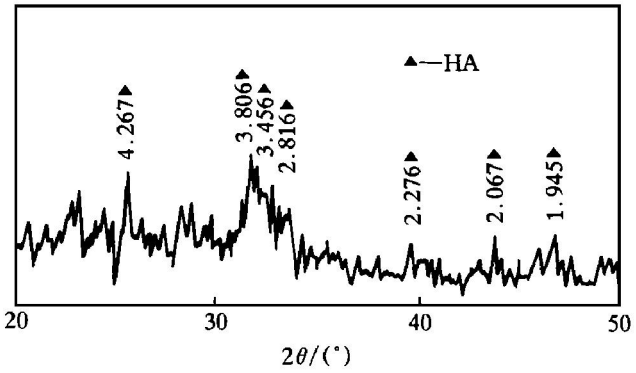

Fig. 2 XRD pattern of modified BG powder

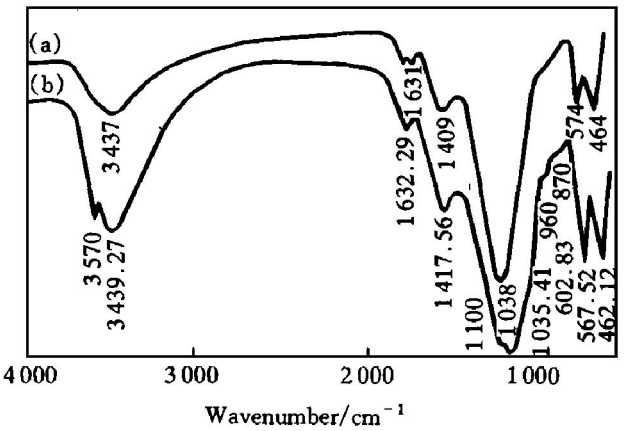

Fig. 3 IR pattern of BG powder
(a) —Pure BG; (b) —BG modified with HA

vibration of O—H in the adsorption H_2O respectively, and the other peaks are caused by different vibration in the $[BO_4]$, $[SiO_4]$ and $[TiO_6]$ of the BG. It can be seen from Fig. 3 that there just exists HA crystal phase and BG glass phase in the modified BG powder. In our previous experiment, it was verified that the electrophoresis deposition of the BG particles unmodified with HA didn't taken place as a result of different charge characteristic on the BG surface. So HA microcrystal is proved to be deposited on the BG surface and it has positive potential in the absolute alcohol medium.

3.2 Surface and cross section appearances of coating

SEM morphologies of the coating and element distribution are shown in Fig. 4 and Fig. 5, respectively. It can be seen that the coating is flat and no obvious flaw. The thickness is about 80μm. The coating bands with the substrate tightly. There exists a clear transition region on the interface and a graded distribution of elements Ca, Si and Ti.

3.3 Composition analysis of coating

The XRD pattern of the coating after sintering at 925 ℃ is shown in Fig. 6. It can be seen that the

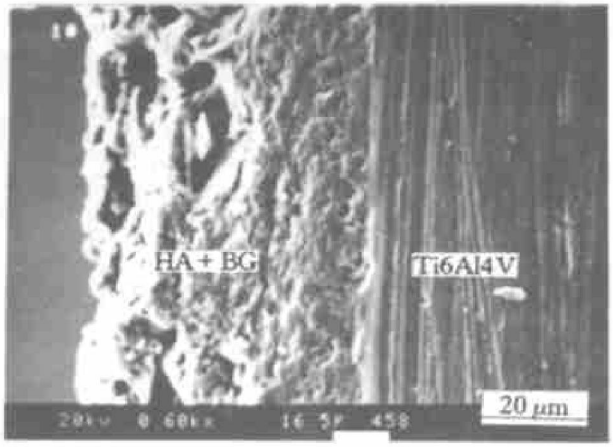

Fig. 4 SEM morpology of coating

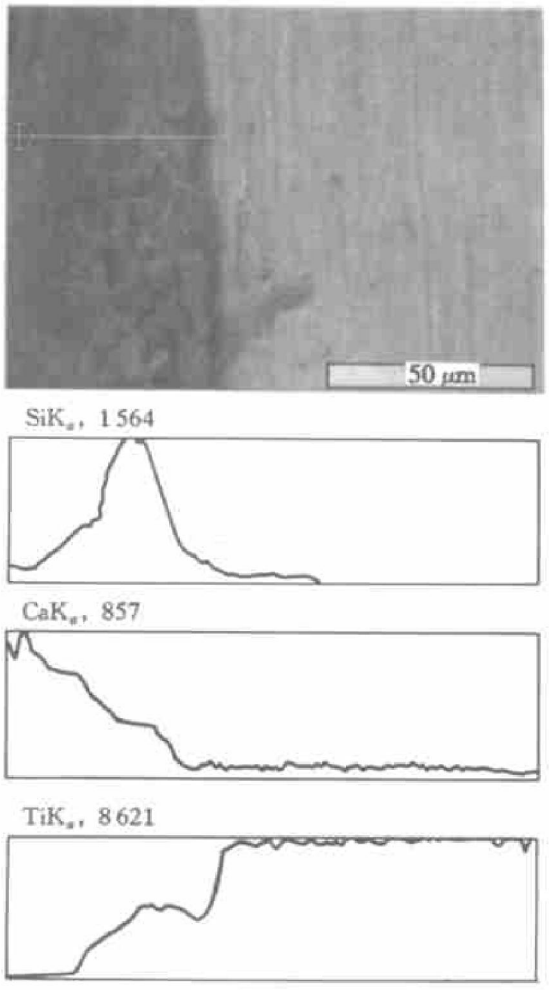

Fig. 5 Distribution of elements on cross section of coating

main crystal phases are HA and CaTi[SiO_4]O, which shows that crystallization occurs in the bioglass phase and CaTi[SiO_4]O is produced[9]. From IR pattern of the modified BG (as shown in Fig. 3), the peak at 462 cm^{-1} corresponds to the stretch vibration of Ti—O in the isolated [TiO_6], which makes out that Ti is a network modified agent, not a network forming agent in the BG. TiO_2 is a good forming agent of crystal nucleus, so titanite CaTi[SiO_4]O forms in the BG phase of the coating.

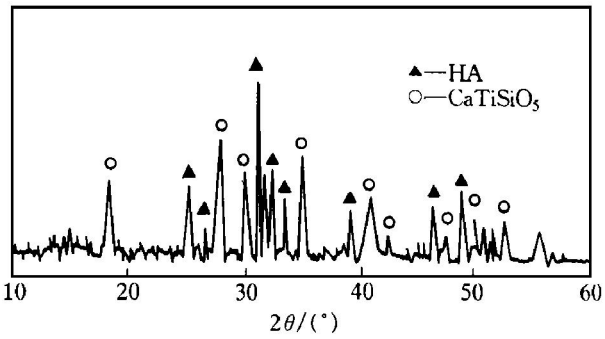

Fig. 6 XRD pattern of coating after sintering

3.4 Relationship between coating thickness and depositing time

It can be seen from Fig. 7 that there is a parabolic relationship between the amount of the deposited coating on the substrate and depositing time. With depositing going on, the electric potential weakens and resistance rises, so that the depositing process is gradually slowed down. The theoretic formula is expressed as follows[11].

$$\sigma = \delta S (R_s^2 + 4kt)^{1/2}/2$$

where σ is the thickness of the coating, S is the area of the electrode, δ is the conductivity of the deposition layer, R_s is the resistance of the suspension, and k is a constant. Fig. 7 shows that the best thickness (50 μm)[12,13] of the coating can be achieved when the depositing time is 4 min.

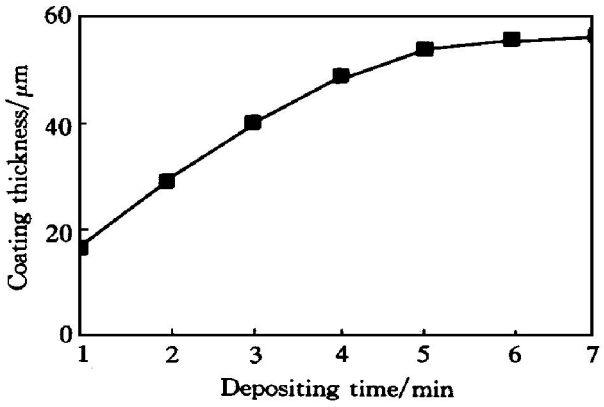

Fig. 7 Relationship between coating thickness and depositing time

3.5 Relationship between adhesive strength and sintering temperature

Adhesive strength between the coating and the substrate was measured by the gluing and tensioning test. The results are shown in Fig. 8 (corresponding depositing time is 4 min). It can be seen that adhesive strength of the coating can reach 18 MPa and the optimal heat treatment temperature is below 925 ℃, at which α phase in the alloy changes into β phase, so the heat treatment has no influence on the mechanical properties of the substrate[14]. The adhesive strength

only reaches 10 MPa when single HA is deposited through the same process. The reason is that the interlayer, made from the sintered modified BG powder, has minor coefficient of thermal expansion ($\alpha = 9.9 \times 10^{-6}/℃$) comparing with that of the substrate. Therefore, after the coating is sintered, a compression stress brings in the coating. It is advantageous for binding of the coating with the substrate. Moreover single HA dose not bind effectively with the substrate if the sintering is carried out at a lower temperature (< 1 000 ℃), and extravagant sintering temperature will lead to an excessive oxidation of the titanium alloy. There exists an obvious transition region (as shown in Fig. 5) on the interface. From the graded distribution of elements Ca, Si and Ti, we can deduce that there exists a graded distribution of BG and HA in the coating. Taking as a high temperature binder, the modified BG near the substrate is beneficial for the binding between the coating and the substrate.

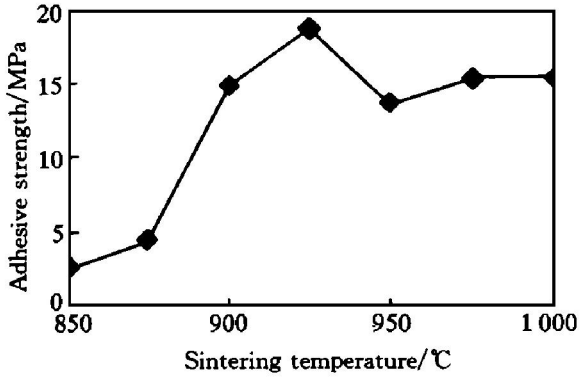

Fig. 8 Relationship between adhesive strength of coating and sintering temperature

4 CONCLUSIONS

1) The modified BG powder is better for preparing graded coating at high temperature. A codeposition of the modified BG and HA on the substrate Ti6Al4V is realized in absolute alcohol mediuum by EPD, and then a bioactive graded ceramic coating Ti6Al4V/BG/HA is obtained after sintering. The adhesive strength of the coating reaches 18 MPa.

2) The better technology parameters of the electrophoresis deposition process are as follows: the depositing voltage is 50 V, depositing time is 5 min. The optimal sintering procedures are got at 925 ℃ for 1 h in argon atmosphere.

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